(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 423 499 A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 90118060.4

(51) Int. Cl.5: B05D 3/06, C08J 7/18

(22) Date of filing: 19.09.90

(30) Priority: 20.09.89 IT 2176489

(43) Date of publication of application:
24.04.91 Bulletin 91/17

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR LI NL SE

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(54) Process for improving the adhesiveness of the surface of articles of polymeric material and articles obtained thereby.

(57) Described is a process for improving the adhesiveness of the surface of articles of polymeric material which comprises irradiating said surface with low-energy electron beams.

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The irradiation time is a function of the characteristic current intensity of the electron beam, but in any case should be such as to supply the irradiated surface with the above amount of energy.

Preferably, the polymeric material used in the process of the present invention is selected from polymers which crosslink when irradiated, and are described in "Crosslinking with Radiation", Encyclopaedia of Polymer Science and Technology, 1986. Examples of such polymers are high-density, medium-density and low-density polyethylene, copolymers of ethylene and propylene and/or butenes, polystyrene, impact-resistant polystyrene, styrene copolymers such as styrene-acrylonitrile resins (SAN), imidized styrene-maleic anhydride resins (SMA), acrylonitrile butadiene-styrene resins (ABS), etc.; polyesters such as poly(ethylene terephthalate), poly(butylene-terephthalate), etc., thermotropic liquid crystals such as poly-(1-phenylethyl-1,4-phenylene-phenyl-1,4-phenylene)-terephthalate, polyacrylates, such as polymethylmethacrylate and polyethylacrylate, etc.

Articles fabricated from a polymeric material whose outer surface has been irradiated with an electron beam at an energy level of not higher than 5 keV, and preferably of from 0.1 to 5 keV, in the presence of a partial oxygen pressure of from 2×10^{-5} to 2×10^{-3} Pa, and preferably of from 2×10^{-4} to 2×10^{-3} Pa, are a further object of the present invention.

A first advantage of the present process is that the electron beam only affects the surface of the irradiated article and, if at all, layers of very limited thickness lying under said external surface.

In fact, at energies of, e.g., 0.2 to 2 keV, the mean free path of the electrons, as reported in a paper by M.P. Seah and W.A. Dench published in "Surface and Interface Analysis" (Volume 1, page 2, 1979) ranges from 1 to 10 nm. As a consequence, the thermomechanical properties of the whole fabricated part remain completely unchanged.

Another advantage of the present invention is that according to the instant process, it is no longer necessary to limit the concentration of oxygen inside the treatment chamber to values which are as low as possible, as taught by the relevant technical literature (US-A-2,955,953), inasmuch as sufficiently high amounts of oxygen, associated with low-energy electron beams, make it possible to control the surface crosslinking reactions.

A further advantage of the process according to the present invention is that it may be carried out on the fabricated polymer part before the coating (e.g., a paint or adhesive layer) is applied to it, in contrast to what is described in the technical literature, e.g., in "Electron Beam Curing of Polymers" (SRI, Menlo Park, 1985) or in GB-A-1,277,674 and 1,264,579.

Furthermore, the effect of the treatment persists over time and at room temperature, whilst when the treatments known from the prior art (US-A-2,955,953) are used, it is recommended that the time elapsing between the treatment and the coating is not longer than five minutes, unless the irradiated part is stored under an inert atmosphere or at a temperature lower than -80 °C.

Finally, as reported, e.g., in the paper by G.A. Senich and R.E. Florin in "Journal of Macromolecular Science - Reviews in Macromolecular Chemistry and Physics", Vol. C24, page 239 (1984), inasmuch as the collisions of high-energy electrons generate very hard X-rays, a good shelter should be provided in order to safeguard the operators. At the energy levels used in the process according to the present invention, such precautions are not necessary.

The products obtained by means of the process according to the present invention may be used with particularly advantageous results in the fields of transportation, electrical appliances for household use, cars, telecommunications, business machines and the like, in order to produce doors, covers, decks, cases, panels, etc.

Another, very useful application is in packaging films, in which the adhesion to other polymeric layers, and the printability are enhanced.

The following examples are to illustrate the present invention without being a limitation of the scope thereof.

In all examples a device was used, which comprised a vacuum chamber having an inner diameter of about 40 cm and a height of about 30 cm. The evacuation of the inner chamber of the reactor was secured by a pumping device capable of reaching pressures of the order of 10^{-6} Pa. To the vacuum chamber an electronic gun (EGG 3H manufactured by Kimball Physics Inc. of Wilton, New Hampshire) was applied, which gun was capable of emitting electrons with energies within the range of from 0.1 to 10 keV, with a current intensity of up to 50 mA. The electrons were emitted with uniform concentration to impinge onto a circular area (radius: 10 cm). The specimen, in the instant case small polymer slabs, were arranged perpendicularly to the electron gun.

In the case of polymeric film the treatment can be carried out continuously. A schematic description of an equipment for the treatment of films with electron beams can be found in US-A-4,533,566.

Example 1

Slabs (6 x 6 x 0.3 cm) produced by injection moulding from high-density polyethylene ERACLENE® QG 6015 (produced by ENICHEM, Milan) were irradiated by using the above equipment, with the total inner pressure being kept at 5 x 10^{-3} Pa (partial pressure of oxygen = about 10^{-3} Pa).

The adhesiveness was measured by means of two methods.

The first method consisted of a test for the determination of tensile strength, carried out by first causing an aluminum punch to adhere to the polymeric surface by means of an epoxy adhesive. The instrument used in order to carry out the measurement is marketed under the name "Sebastian II" by Quad Group of Lewis-Spokane (Washington), which also supplied the aluminum punches coated with epoxy resin, capable of withstanding tensile stresses of up to 700 kg/cm^2.

The second method consisted in subjecting the specimen of polyethylene, treated and bonded, to shear stress. The adhesive junctures were prepared according to ASTM D 1002-72, using a commercially available epoxy adhesive (E11 manufactured by Permabond of Bridgewater, New Jersey) and were crosslinked for one hour at 90 °C, as recommended by the manufacturer of the adhesive. The shear stress was applied by using a TMSM model electromechanical dynamometer manufactured by Instron according to the conditions called for by ASTM D 1002-72.

In Table 1, the experimental parameters of the treatment and the obtained results in terms of adhesiveness are reported.

It can be seen that with energy amounts of more than 1.5 J/cm^2 further increases in tensile strength are not obtained. The obtained values may be compared to the tensile strength values of high-density polyethylene, which range from 270 to 330 kg/cm^2, as reported in Encyclopaedia of Modern Plastics (McGraw-Hill, New York, 1988), page 537. Therefore, in order to cause breakage of the adhesive-bonded juncture, a stress close to the tensile strength of high-density polyethylene is necessary, a result which indicates that a breakage of the cohesive type occurs in the interior of the material.

Table 1

Energy of electrons (eV)	Current intensity of electron beam (mA)	Treatment time (seconds)	Energy supplied per unit surface area (J/cm^2)	Tensile strength (kg/cm^2)	Shear strength (N/mm^2)
200	2	60	0.3	44.2	
200	2	300	1.5	181.3	1.03
200	2	1,200	6.1	181.3	
1,000	10	30	3.8	165.7	
1,000	10	60	7.6	181.8	
1,000	2	30	0.8	118.0	
1,000	20	30	7.6	182.5	1.46
0				0	0.43

In Table 2 the results which were obtained when the total pressure inside the irradiation chamber was lowered to 1 x 10^{-4} Pa (partial pressure of oxygen 2 x 10^{-5} Pa) are reported. As one can see, the tensile strength values are much lower, which shows that the control of the crosslinking by the oxygen contained inside the chamber is important for the tensile strength of the bonded juncture.

Table 2

Energy of Electrons (eV)	Current intensity of Electron beam (mA)	Treatment time (seconds)	Energy supplied per unit surface area (J/cm^2)	Tensile strength (kg/cm^2)
200	2	300	1.5	67.1
1,000	10	30	3.8	73.5

Table 5

Energy of electrons (eV)	Current intensity of Electron beam (mA)	Treatment time (seconds)	Energy supplied per unit surface area (J/cm^2)	Tensile strength (kg/cm^2)
1,000 0	20	30	7.6	162.52 44.7

Claims

1. Process for improving the adhesiveness of the surface of articles made of polymeric material, comprising irradiating said surface with an electron beam of an energy not higher than 5 keV in the presence of oxygen at a partial pressure of from 2×10^{-5} to 2×10^{-3} Pa.
2. Process according to claim 1, wherein the electron beam has an energy of from 0.1 to 5 keV.
3. Process according to claim 2, wherein the electron beam has an energy of from 0.2 to 2 keV.
4. Process according to any one of the preceding claims, wherein the partial pressure of oxygen ranges from 2×10^{-4} to 2×10^{-3} Pa.
5. Process according to any one of the preceding claims, wherein the amount of energy emitted per unit of irradiated surface area is from 0.1 to 1.5 J/cm^2.
6. Process according to any one of the preceding claims, wherein the polymeric material is a polymer which is capable of crosslinking when irradiated.
7. Articles obtainable by the process according to any one of the preceding claims.
8. Use of the articles according to claim 7 for manufacturing films, doors, covers, decks, cases, panels for use in the fields of transportation, electrical appliances for household use, cars, telecommunications, business machines and packaging.